NEW APPLICATIONS OF THE FILM BALANCE

BY
FRANK McLERAN RUGG
B.A., Mississippi College, 1933
M.S., Louisiana State University, 1935

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FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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PART I

SPREADABILITY: ITS MEASUREMENT AND APPLICATION TO THE STUDY OF SULFURIZED OIL

Introduction

The principal use for which the film balance[1,2] has been employed thus far is the study of materials which form monomolecular layers on water. Not only is the balance applicable to the study of such materials but it is also applicable to the study of materials which form multimolecular layers or lenses on water.

Wyatt[3] has used the film balance in studying the deterioration of power cable oils by determining the spreads of a given volume of benzene solutions of these oils. The exact technic as used by Wyatt was not clearly discerned from the literature, but owing to the possibility of contamination from the sides of the trough as a result of solvent action of the benzene and the inability to follow accurately the changes of the hydrophilic properties of a given film with time, it was decided that for general use and more accurate measurements, the spread of a film of the material itself in the absence of a solvent would be much more satisfactory. Such a film can be readily obtained since a drop of benzene containing a slightly hydrophilic substance at a concentration of 6×10^{-4} g. per ml. will evaporate in approximately two seconds.

In this investigation the film balance was found to be especially adapted to the study of the effects of various treatments on the hydrophilic properties of those materials which form multimolecular layers or lenses on water. The hydrophilic property of a material is expressed as a "spreadability" value which is that area into which a given weight of material, when spread on water, is compressed by a force of 1.35 dynes per cm. (a value arbitrarily chosen since it corresponds to 5 scale divisions on the balance).

It is significant that the spreadability of some materials which may undergo oxidation or some other type of chemical change may be increased by as much as 4000% in a short time. This enormous increase in spreadability is readily understood when one considers the fact that

a non-hydrophilic substance which will form a film an average of 50 or more molecules thick when compressed by a force of 1.35 dynes per cm. on a water surface will, under this same pressure, become monomolecular if each molecule is made only slightly hydrophilic.

The effects of various types of radiation under various conditions on the hydrophilic properties of oils have been determined in this study by using this new technic and by observing the increase in area covered by a lens on water.

Experimental

All spreadability values were measured on the Cenco "Hydrophil Balance"[4].

The spreadability of an oil is determined by (1) diluting the oil with benzene, (2) adding a known weight of the oil onto the surface of the water contained in the balance, (3) compressing the film until a force of 1.35 dynes per cm. is registered, and (4) recording the area occupied by the film under pressure. In carrying out the second step the benzene solution of the oil is added drop by drop allowing time between drops for the benzene to evaporate.

The apparatus used in determining the behavior of lenses on water in air or in an atmosphere of nitrogen consisted of (1) an absorption train for complete removal of oxygen from nitrogen, (2) a source of ultra-violet radiation, and (3) a crystallizing dish which was provided with a transparent quartz cover and four side-arms. Three of the side-arms were used as gas inlets and outlets. A glass rod was placed in the fourth. From one end of this rod and at right angles to it a stem was drawn out. From this stem the lenses of the oils studied were deposited on the water in the dish. The dish was placed on graph paper so that the increase in diameter of the lenses could be readily followed.

Experimental Results

All results are best indicated graphically, since curves express the true course of events. From these curves the folowing typical observations may be cited.

1. The spreadabilities of two sulfur-containing oils and the parent unsaturated oil were increased enormously (1200% and more) by ex-

posing their benzene solutions to either white light (RAD.E), ultra-violet light having a short wavelength limit of 3000 A (RAD.C), or ultra-violet light with a short wavelength limit of 2500 A (RAD.B).

2. Irradiating benzene solutions of a lubricating oil, liquid paraffin, and synthetic drying oil (diethylene-acetylene) with RAD.C did not appreciably alter their spreadabilities.

3. Films (lenses) of the unsaturated oil, sulfur-containing oils, and lubricating oil were deposited on the surface of the water in the balance and exposed to RAD.B. Four minutes of this irradiation increased their spreadabilities 750% and more.

4. The rates of increase in area occupied by lenses on water of each of the oils mentioned in 3 above were decidedly different under each of the following conditions: (1) lenses on distilled water in the presence of air and exposed to RAD.B, (2) lenses on oxygen-free water in an atmosphere of oxygen-free nitrogen and likewise exposed to RAD.B, (3) lenses on oxygen-free water in oxygen-free nitrogen without irradiation, and (4) lenses standing on distilled water exposed to air and again without irradiation.

5. Films of the lubricating oil, lubricating oil plus 5% methyl dichlorostearate, oil containing 5.7% sulfur, and the sulfur-containing oil to which had been added 5% of the chlorinated ester were deposited on the water surface and allowed to stand exposed to air for several hours. Spreadability values were obtained at regular intervals. It was found that in each case the rate of increase in spreadability was very small and that the presence of the ester greatly increased the original spreadability.

6. The effect of RAD.C on the spreadability of oil containing 8.4% sulfur in bulk was enhanced by the presence of brass rods, but that even in the presence of the metal 13 days of this irradiation only increased its spreadability approximately 75%.

7. The effect of RAD.B on the unsaturated oil and the sulfurized oil containing 8.4% sulfur was determined by irradiating their benzene solutions and obtaining pressure-area curves at intervals. These curves obtained after irradiation are markedly displaced toward greater area values, especially for low pressures, from those for the original unirradiated materials.

PART II

SPREADING PRESSURE: ITS MEASUREMENT AND APPLICATION TO THE STUDY OF VEGETABLE OILS, PAINTS, AND LUBRICATION ADDITION AGENTS

Introduction and Theory

A method for measuring the extent to which oxidation has taken place in a vegetable oil was recently proposed by Marzolf[5]. This method consists in determining the minimum concentration of a freshly poured soap soultion which will, after lapse of a constant period of time, prevent rapid spreading of a drop of the oil when placed on the surface of the solution. Having already observed that a drop of benzene would not spread on water covered with a monomolecular film under considerable pressure and also having observed that a solution of Dreft quickly forms a surface film of considerable pressure, it was suspected that film pressure, and not film composition was the important feature in determining whether or not benzene, vegetable oil, or any similar liquid would spread on water covered by a film of some contaminant. This proved to be the case for soybean oil, linseed oil, and several lubrication addition agents and it is thought to be true for any liquid, a drop of which will spread on water.

The literature revealed that Washburn and Keim[6] had found this to be true for volatile organic liquids and that Murray[7] had found it to be true for mineral oils containing hydrophilic substances.

Harkins and Feldman[8] have given a very simple expression,

$$S = W_a - W_c,$$

for the free energy change, S, which occurs when a drop (lens) spreads on water. Considering the case of an oil drop on water W_a represents the work of adhesion which is the energy that must be expended in separating unit surface of the oil from unit surface of the water. W_c is the term for the work of cohesion which is the expenditure of energy necessary in creating two unit surfaces of oil. The units of S are ergs per sq. cm., but since the values of S are numerically equal to the spreading pressure (force) of the oil lens in dynes per cm., these will be referred to in this report as spreading pressures. Since oxidizing an oil increases its spreading pressure, a technic for measuring this pressure

(force) would obviously serve as an empirical method for measuring the extent of oxidation in such a liquid.

Experimental

The technic employed in the measurement of these spreading pressures involved the following operations: (1) Obtaining a monomolecular film of oleic acid on the surface of the water contained in the hydrophil balance[4], (2) decreasing the area covered by the oleic acid, by advancing the film barrier, until the film gives a pressure of approximately 25 dynes per cm., (3) adding a drop of the oil in question to the film covered surface, and (4) withdrawing the barrier until the film pressure becomes constant. This constant pressure is, at least effectively, the spreading pressure of the oil.

In the study of vegetable oil and paints peroxide numbers were obtained and compared to their spreading pressure values. The technic used in determining the peroxide numbers is given by Wheeler.[9]

Experimental Results

Spreading pressure values of several liquid lubrication addition agents were obtained. Such values are considered important since they represent the free energy decrease in ergs per sq. cm. accompanying the formation of a monomolecular film. These data in dynes per cm. appear below in tabular form.

Methyl ricinoleate	23.10
Methyl dichlororicinoleate	22.15
Methyl oleate	27.80
Methyl dichlorooleate	28.30
Methyl dichlorostearate	19.30
Methyl tetrachlorostearate	21.90
Methyl α-chloromyristate	23.80
Glycol ricinoleate	27.55
Tricresyl phosphate	7.55
"Ortholeum" Four-Ten	20.45

Data representative of that obtained in the study of vegetable oils and paints are given below. These values were obtained by blowing the

materials indicated with oxygen in light and in dark at a temperature of 26 ± 2° C (air blowing at 100° C for soybean oil), and determining the spreading pressure values and peroxide numbers at the specified intervals. Such data demonstrate the applicability of this technic as an empirical method for measuring the extent of oxidation in such materials. For example, the data show a maximum in the peroxide number of oxidized soybean oil followed by a marked decrease while the spreading pressure values rise continuously with time of blowing.

Material	Time of Blowing in Hours	Peroxide No.		Spreading Pressure (scale units)*	
		Light	Dark	Light	Dark
Alkali Refined	0.00		9.44		44.4
Soybean Oil	8.50		135.2		65.8
	23.75		249.0		84.1
	42.75		72.74		88.5
Alkali Refined	00.0	28.56	28.56	72.8	72.8
Linseed Oil	25.0	47.40	37.36	74.7	73.4
	75.0	126.7	55.05	76.0	74.7
	144.0	554.7	81.45	80.6	74.9
	336.0	1281.	328.3	91.3	79.7
	672.0	1691.	1671.	98.5	92.5
Alkali Refined	00.0	1.04	1.04	52.8	52.8
Linseed Oil &	144.0	105.7	62.12	62.0	60.2
TiO_2 Pigment	336.0	495.9	250.8	80.1	72.5
	672.0	773.0	557.1	91.0	89.3
Alkali Refined	00.0	2.38	2.38	64.0	64.0
Linseed Oil &	48.0	11.02	6.08	66.0	64.7
ZnS Pigment	144.0	47.81	20.82	72.1	66.5
	336.0	382.5	266.0	83.0	78.8
	672.0	807.1	470.0	94.3	96.7

* To convert to dynes per cm. multiply by 0.270.

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VITA

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